



Yan, C., Sagisaka, M., James, C., Rogers, S. E., Peach, J., Hopkins Hatzopoulos, M., & Eastoe, J. (2015). Action of hydrotropes in water-in-CO₂ microemulsions. *Colloids and Surfaces A. Physicochemical and Engineering Aspects*, 476, 76-82.
<https://doi.org/10.1016/j.colsurfa.2015.03.010>

Peer reviewed version

License (if available):
CC BY-NC-ND

Link to published version (if available):
[10.1016/j.colsurfa.2015.03.010](https://doi.org/10.1016/j.colsurfa.2015.03.010)

[Link to publication record in Explore Bristol Research](#)
PDF-document

This is the author accepted manuscript (AAM). The final published version (version of record) is available online via Elsevier at <http://dx.doi.org/10.1016/j.colsurfa.2015.03.010>. Please refer to any applicable terms of use of the publisher.

University of Bristol - Explore Bristol Research

General rights

This document is made available in accordance with publisher policies. Please cite only the published version using the reference above. Full terms of use are available:
<http://www.bristol.ac.uk/red/research-policy/pure/user-guides/ebr-terms/>

Action of hydrotropes in water-in-CO₂ microemulsions

Ci Yan[◇], Masanobu Sagisaka[†], Craig James[†], Sarah Rogers[§], Jocelyn Peach[◇] and Julian Eastoe^{◇*}

[◇]School of Chemistry, University of Bristol, Bristol BS8 1TS, United Kingdom

[†] Department of Materials Science and Technology, Faculty of Science and Technology, Hirosaki University, Bunkyo-cho 3, Hirosaki, Aomori 036-8561, Japan

[§] Rutherford Appleton Laboratory, ISIS Facility, Chilton, Oxfordshire OX11 0QX, United Kingdom

* To whom correspondence should be addressed. E-mail: Julian.eastoe@bris.ac.uk

Abstract

The effects of a homologous series of sodium p-n-alkylbenzoate hydrotropes in water-in-supercritical CO₂ (w/c) microemulsions have been investigated, by comparing the phase behaviour and droplet structures obtained using small-angle neutron scattering (SANS). The w/c microemulsions appeared to be generally stable upon addition of hydrotropes, however, on increasing the alkyl chain length of the hydrocarbon and fluorocarbon moieties of the surfactants, different effects on stability were observed. Using high-pressure SANS (HP-SANS), the effects of hydrotrope type on the structures of microemulsion droplets were studied. Interestingly, evidence was found for multiple shell structures with a hydrotrope rich layer between the water cores and the surfactant films. Such findings are significant to the understanding of self-assembly of co-adsorbed species in supercritical CO₂ (scCO₂), as the hydrotrope layers potentially have significant effects on surfactant packing, and can modify the physico-chemical properties of scCO₂ through formation of worm-like micellar assemblies.

Keywords: microemulsions, supercritical CO₂, hydrotropes, fluorinated surfactants, shape transition, small-angle neutron scattering

1. Introduction

Being nontoxic, non-flammable, and inexpensive, supercritical CO₂ (scCO₂) has received considerable attention as an attractive substitute to normal petrochemical solvents; one of the potential applications of scCO₂ is enhanced oil recovery (CO₂-EOR) of crude oil from porous rock.^{1,2} However, due to the low viscosity liquid CO₂ does not readily facilitate transport to oil bearing rock, but rather through surrounding porous media which offers pathways of least resistance.^{3, 4, 5} To overcome such limitations, different techniques have been investigated to improve the CO₂ mobility and conformance such as CO₂ thickeners,^{6, 7} conformance control gels and in depth mobility control of CO₂ foams assisted by various stabilizers.^{8, 9, 10}

One of the great challenges in the field is addressing the fact that scCO₂ is a poor medium for most commercially available surfactants which have been developed for alkane solvent (e.g. AOT).¹¹ And even for those specifically designed surfactants that effectively stabilise water-in-CO₂ (w/c) microemulsions, modification of the self-assembled structures, which has been well-established as an effective method to enhance the viscosity in alkane solvent, is generally inhibited in scCO₂.

In one of the very few reports on anisotropic self-assembled structures in scCO₂, it was found that by exchanging the surfactant counter ion Na⁺ with divalent species such as Co²⁺ and Ni²⁺, a sphere-rod shape transition can be obtained for the micelles formed not only in alkane solvents with hydrocarbon surfactants,¹² but also in scCO₂.⁴ However, the shape transitions were only observed at very low water content with water: surfactant molar ratio ($W = [\text{water}]/[\text{surf}] \leq 10$), and furthermore, micelles formulated by the counter-ion exchanged surfactants generally require a relatively high pressures (~300 bar) to be

1 stabilised in scCO₂. These factors have largely limited practical applications to modify scCO₂
2 viscosity using this approach.

3 Hydrotropes are small amphiphilic molecules with hydrophilic character, having the ability
4 to increase solubility of organic compounds in water. Hydrotropes have attracted great
5 industrial interest as additives, especially for boosting efficiencies of surfactants in both
6 aqueous and oil phases.^{13,14} Hatzopoulos et al. have conducted a series of studies to
7 investigate the links between the properties of hydrotropes and surfactants with a
8 systematic variation of the molecular structures.^{15,16} Interesting shape transitions between
9 spherical-cylindrical structures have been reported for a number of AOT stabilised water-in-
10 oil (w/o) microemulsions on addition of certain hydrotropes. In recent work,¹⁷ effects of
11 such hydrotrope additives have been investigated with a custom-made tri-chain
12 hydrocarbon CO₂-active surfactant (TC14), and using High-Pressure Small-angle neutron
13 scattering (HP-SANS) elliptical micelles were confirmed for microemulsions in both alkane
14 solvents and scCO₂. That initial study is significant in the development of viscosity modifiers
15 for applications in scCO₂, not only because it represents a new approach to promote
16 micellar growth, but also because the same general effects of hydrotropes are found in both
17 water-in-oil (w/o) and water-in-CO₂ (w/c) microemulsions.

18 In this paper, effects of hydrotropes in w/c microemulsions were further investigated by in-
19 depth SANS studies using selective contrast variation to reveal core-shell internal micellar
20 structures. Although hydrocarbon surfactants are more economically viable and
21 environmental friendly,^{18,19} fluorocarbon surfactants have been applied here to formulate
22 w/c microemulsions, owing to following considerations: firstly, fluorocarbon surfactants
23 offer a much higher stabilisation of w/c microemulsions, which allows the behaviour of
24 hydrotrope molecules to be studied in a well-defined aqueous core structures;²⁰ secondly,

core-shell SANS contrast can be enhanced when a fluorocarbon surfactant shell is present. Lastly, by employing the hydrocarbon-fluorocarbon mixed systems, the generality for the behaviour of hydrotropes with CO₂-philic surfactants can be further tested.

2. Experimental

2.1 Materials and compositions: The structures of surfactants and hydrotropes studied here can be found in Table 1. The details of surfactant synthesis, purification and characterization have been described elsewhere.^{21, 22} The surfactants were used at constant molarity (0.017 mol L⁻¹ in a 0.02 L cell), the hydrotropes were dissolved in water with mixed H₂O and D₂O at fixed concentrations of [hydrotrope]=0.23 mol L⁻¹ and 0.46 mol L⁻¹. An appropriate aqueous solution of the hydrotrope was then introduced to the cell with a fixed water: surfactant ratio $W = [\text{water}]/[\text{surf}] = 15$.

Compounds	Structure
nFS(EO) ₂	
nFG(EO) ₂	
Sodium Benzoate (BenzC ₀)	
Hydrotrope BenzC _n	

2 **Table 1. Structures of the surfactants and hydrotropes used in this study.**

3 For experiments as a function of CO₂ bulk density, the volume fraction (vol. %) of the
4 microemulsions may be slightly different as the cell volume is also varied to achieve
5 different pressures: vol. % = 0.017 at P=350 bar, vol. % = 0.015 at P=200 bar, and vol. % =
6 0.014 at P=160 bar, with the temperature remaining as constant T=45°C, the resulting CO₂
7 density can be calculated using Span-Wagner equation of state and varies within the range
8 $\rho_{\text{CO}_2} = 0.91 \sim 0.71 \text{ g cm}^{-3}$.²³

9 **2.2 Pressure cell:** All samples were studied in a stainless steel cell with variable volume (12-
10 20 mL) controlled by a piston with an external hydraulic pump. Once filled with CO₂, the
11 pressure was measured by a built-in pressure transducer with accuracy ± 1 bar. Two sapphire

windows fitted in parallel allow for visual observations of phase behavior. Temperature was controlled at 45 °C by a water bath flowing around a heating circuit in the cell body. In order to obtain w/c microemulsions, the appropriate amount of pre-weighed surfactant and hydrotrope solution in D₂O/H₂O was fed into the cell to establish the W (= [water]/[surf]) of interest. Subsequently, the cell was sealed and liquid CO₂ was introduced at relatively low temperature ~5°C and re-equilibrated at 45°C in the cell under magnetic stirring. The inlet line was closed once the pressure reached 120 bar, and under these conditions CO₂ is in the supercritical state. The pressure could be further increased using a hydraulic pump, up to a maximum of 450 (±5) bar, which allowed stable w/c microemulsions to be formulated.

2.3 SANS: SANS experiments were carried on the SANS2D instrument²⁴ at the ISIS spallation source, Rutherford Laboratory, UK. SANS2D spans a Q range of 0.002 < Q < 1 Å⁻¹ with neutron wavelength λ of 2.2-10 Å⁻¹.

The transfer of momentum, or scattering vector Q is defined as

$$Q = \frac{4\pi}{\lambda} \sin \frac{\theta}{2} \quad (1)$$

where θ is the scattering angle and λ the incident neutron wavelength.

The scattering data were normalized for the sample transmission, empty cell and solvent background and put on an absolute intensity I(Q)/cm⁻¹ scale using standard procedures, the errors in intensity I(Q) are expected to be lower than 5%.²⁵

The scattering intensity I(Q) is plotted as a function of Q,²⁶ which can be broadly described by:

$$I(Q) \propto P(Q)S(Q) + B_{inc} \quad (2)$$

B_{inc} is the background incoherent scattering, $S(Q)$ is the structure factor related to interparticle interactions. In this study, the systems were at low concentration in a non-polar medium, therefore, at a first approximation $S(Q)$ can be neglected (~ 1).

$P(Q)$ is the form factor which describes the internal structure of scattering particles. It should be noted that, by varying the scattering contrast which arises from the difference in scattering length density (SLD) between adjacent phases, the scattering profile can be altered depending on which region is 'highlighted'. In order to study the effect of hydrocarbon additives on fluorocarbon surfactant films in w/c microemulsions, a core-shell contrast was employed to highlight the different local domains, as described in ref. 20.

The data have been analysed by the fitting program SASview using a built-in spherical core-shell form factor model.^{27,28} The scattering laws used can be found in Supporting information, the SLD of the water core and CO₂ bulk were calculated from their compositions and constrained for the purposes of fitting (with 30 wt% D₂O and 70 wt% H₂O, $SLD_{core}=1.5 \times 10^{-6} \text{ \AA}^{-2}$; $SLD_{CO_2}=1.8 \times 10^{-6} \text{ \AA}^{-2}$ when $\rho_{CO_2}=0.71 \text{ g cm}^{-3}$, and $2.3 \times 10^{-6} \text{ \AA}^{-2}$ when $\rho_{CO_2}=0.92 \text{ g cm}^{-3}$). The SLDs of different hydrotropes are: $SLD_{C_0Benz}=1.5 \times 10^{-6} \text{ \AA}^{-2}$, $SLD_{C_2Benz}=1.3 \times 10^{-6} \text{ \AA}^{-2}$, and $SLD_{C_8Benz}=0.85 \times 10^{-6} \text{ \AA}^{-2}$, which are relatively close that for the mixed D-H water core.

In addition, the maximum concentration of additives in the aqueous cores is $< 0.5 \text{ mol L}^{-1}$, which should have no notable effect on the "volume fraction". Therefore, addition of hydrotropes should not have any significant impact on the value of SLD_{core} . On the other hand, due to the unknown influence of hydrotropes on surfactant packing, the SLD of surfactant layer, or the shell, is difficult to predict. However, the surfactant chain length (or the shell thickness) is expected to be unaffected by the presence of these additives, and can

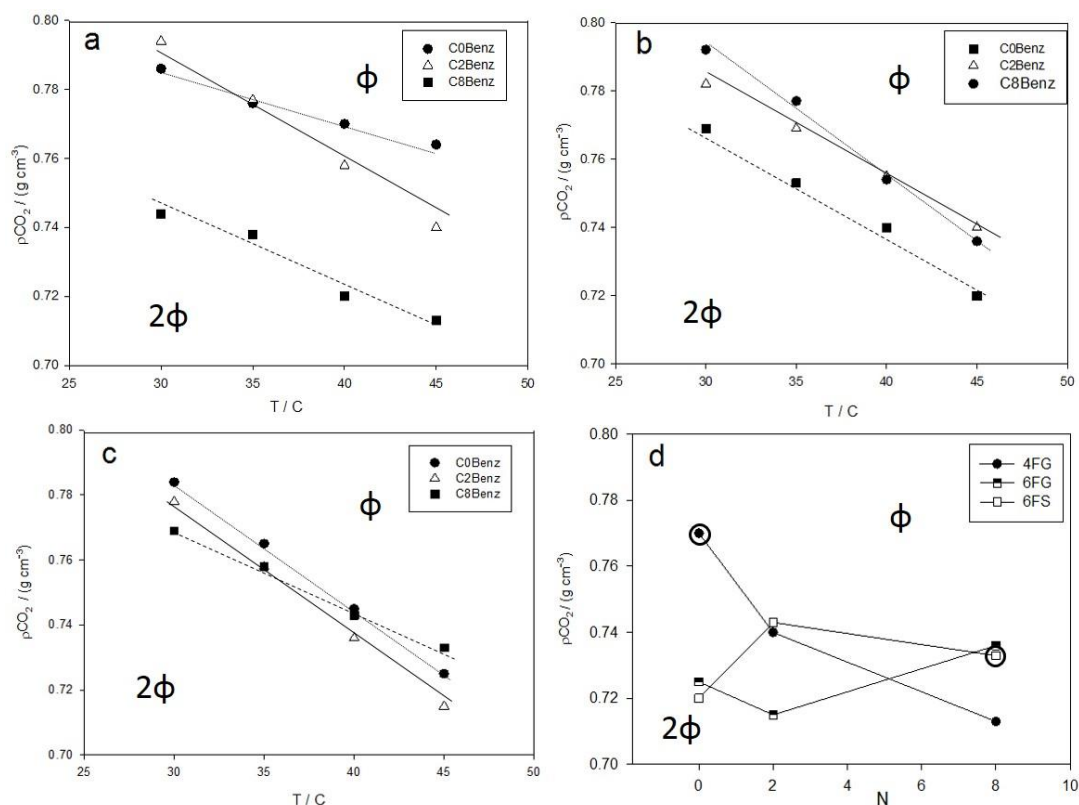
1 be treated as a constrained parameter. For this study, the shell thickness for each surfactant
2 was correspondingly obtained from the hydrotrope free w/c microemulsions, with the SLD
3 value calculated from the structure and density of an equivalent fluoroalcohol with same
4 number of CF₂ units ($SLD_{shell} \sim 3.5 \times 10^{-6} \text{ \AA}^{-2}$), the results show essentially identical shell
5 thicknesses for 6FG(EO)₂ and 6FS(EO)₂ $\sim 8 \text{ \AA}$, whereas for 4FG(EO)₂, the shell thickness is ~ 6
6 \AA . These parameters were then fixed in the analyses of systems with added hydrotropes,
7 with the SLD_{shell} being allowed to adjust within a sensible range (3×10^{-6} to $4 \times 10^{-6} \text{ \AA}^{-2}$).

8

3. Results and discussion

3.1 Phase behaviour: The phase behaviour of the w/c microemulsions at W15 with C_n Benz additives has been studied via visual observation at as a function of temperature and pressure, and the results are summarised in Figure 1. In general, turbid-transparent phase transitions have been observed for all the samples, however, for two of the mixtures: 4FG(EO)₂+C₀Benz and 6FS(EO)₂+C₈Benz, although such phase transitions were still observed, the systems appeared to coexist with significant amount of undissolved droplets, even at the highest pressure up to 400 bar. Nevertheless, the results (Figure 1a, 1b, 1c) have clearly revealed that the CO₂ density at the phase boundary decreases linearly with temperature.

1



2

3 **Figure 1 Phase behaviour of w/c microemulsions at W15 stabilised by 4FG(EO)₂, 6FS(EO)₂**
 4 **and 6FG(EO)₂ surfactants (in figure a, b and c respectively) after mixing with different**
 5 **hydrotropes. The measured phase transition pressures-temperatures have been**
 6 **converted to the corresponding CO₂ densities. In Figure 1d, the effect of hydrotrope**
 7 **chainlength are compared for each surfactant at 45 °C by plotting the alkyl carbon number**
 8 **N against the CO₂ density at the phase transition point. It should be noted again that, for**
 9 **the circled data points, the system actually appeared to be transparent but coexisted with**
 10 **droplets, instead of a clear single phase as the others.**

11 In Figure 1d, the stability of the w/c microemulsions have been cross compared at 45 °C, and
 12 all three surfactants appeared to exhibit very different behaviour as a function of
 13 hydrotrope chain length N. For the systems with 6FG(EO)₂, the effect of hydrotrope

additives appeared to be relatively mild, whereas a more significant destabilisation, as indicated by the increasing CO₂ density at the phase transition point is seen for 6FS(EO)₂ stabilised systems as N increases. Interestingly, for 4FG(EO)₂ stabilised systems, variation of N also appeared to give significant effects, but with the opposite trend compared to 6FS(EO)₂: as shown in the figure, with a long chain hydrotrope, C₈Benz, the stabilisation point for 4FG(EO)₂ system was obtained at much lower CO₂ density, but with a more hydrophilic additive (i.e. C₀Benz or C₂Benz), the stabilisation pressure/density increases, hence, the system become less stable.

3.2 Hydrotropes with 6FG(EO)₂ and 6FS(EO)₂: Studies based on water-in-oil (w/o)

microemulsions have demonstrated that the effect on the structure of microemulsion droplets varies with the chain length N of hydrotrope additives.^{15, 16} In Figure 2a, the SANS from 6FS(EO)₂ stabilised microemulsions with short chain C_nBenz additives (n=0, 2) at 350 bar are compared, and the main fitting parameters are listed in Table 2. The shift of scattering profiles for both C₀ and C₂Benz added systems clearly indicates a small reduction in the core radius (R_{core}), from 18 Å for a hydrotrope free microemulsion, to ~15 Å on average as C₀Benz and C₂Benz hydrotropes were added. Moreover, an interesting dependence between the size polydispersity of microemulsion droplets and hydrotrope concentration was also observed: at lower hydrotrope molar concentration ($M=0.23 \text{ mol L}^{-1}$, $M_{\text{hydrotrope}}: M_{\text{surfactant}} \sim 1:16$), the polydispersities were found ~25%. With increased hydrotrope concentration (0.46 mol L^{-1} , $M_{\text{hydrotrope}}: M_{\text{surfactant}} \sim 1:8$), however, the polydispersity dropped to 18%, which was equivalent to the hydrotrope free microemulsion. As suggested by a number of studies,^{29, 30} variation in the microemulsion size polydispersity can be interpreted in the framework of film bending energy theory: details of the

correlation between polydispersity and film bending energies can be found in the Supporting Information for this paper.

The reduction in microemulsion radius found in these systems could be explained by the effect of increased charge screening at the headgroups,³¹ and increased entropy of mixing due to addition of hydrotropes, the film bending energy initially decreases, as indicated by the increase of the size polydispersity compared to hydrotrope free system. As the charge screening becomes more significant with increasing hydrotrope concentration, surfactant films appear to become more rigid, and the polydispersity decreases.

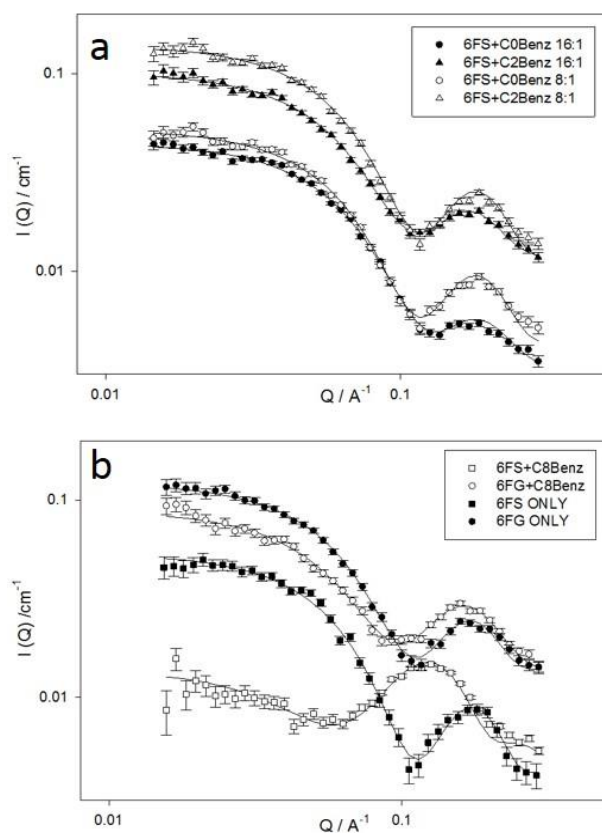
On the other hand, once a longer chain hydrotrope, C₈Benz, was introduced at concentration 0.23 mol L⁻¹ to the aqueous core, both the structure and stability of w/c microemulsion were found be significantly different: instead of stable single phase microemulsions, the systems appear to coexist with an extra phase, which can be seen by SANS from the sharply increased intensity at low Q range. More importantly, a significant enhancement of intensity was also found for the mid-Q range the peak, and the scattering profile is not consistent with the core-shell model as seen for the 6FS(EO)₂ stabilised w/c microemulsions (See Supporting Information). In a previous contrast variation SANS study of w/c microemulsions, it was demonstrated that such enhancement could be obtained as a result of increased definition of the core-shell boundary,²⁰ such as a reduction in SLD_{core}. Although in an earlier section, it was noted that the hydrotropes dispersed in the aqueous cores should not have any significant effects on the value of SLD_{core}. However, as an amphiphilic molecule, C₈Benz is very likely to accumulate at the water/CO₂ interface. The SANS results seem to suggest that, instead of mixing towards the fluorocarbon shell which would should result in a reduction in core-shell contrast, a hydrocarbon-rich layer has been

1 formed, which causes a change at the core-shell interface. Hence, a core multi-shell model
2 has been applied to analyse these data, with a hydrotrope rich layers as extra shells
3 between the H₂O/D₂O cores and the fluorocarbon shells. The SLD_{hydrotrope-layer} was set to
4 $0.95 \times 10^{-6} \text{ \AA}^2$, based on the SLD of C₈Benz with assumptions that the hydrotrope layer
5 coexists with 20 wt% H₂O/D₂O of the aqueous core. Good agreement was obtained between
6 the multi-shell model and the scattering profile as shown in Figure 2b, and the fitting
7 parameters are listed in Table 2.

8 It should be noted that, although a hydrocarbon moiety is also found in 6FS(EO)₂ surfactant
9 itself, interestingly, a multiple-shell scattering profile has never been observed in any other
10 w/c microemulsions reported. This is possibly due to hydration of the headgroups, and also
11 the weak contrast in such systems.

12

1



2

3 **Figure 2a (upper) shows the SANS results for 6FS(EO)₂ and 6FG(EO)₂ stabilised**
 4 **microemulsions with short chain hydrotropes (C₀ and C₂Benz). The datasets have been**
 5 **multiplied by factors of 1.5× for 6FS+C₀Benz at 8:1, 3× for 6FS+C₂Benz at 16:1 and 4× for**
 6 **6FS+C₂Benz at 8:1. Figure 2b (lower) compares the effect of a longer chain hydrotrope**
 7 **(C₈Benz) on w/c microemulsions with 6FS and FG(EO)₂, in comparison to the w/c**
 8 **microemulsions without hydrotropes . The datasets for 6FG+C₈Benz have been multiplied**
 9 **by 3×, and 6FG(EO)₂-only system by 4×.**

10 The interactions between the hydrocarbon moieties of surfactant and hydrotropes was
 11 further investigated in w/c microemulsions stabilised by 6FG(EO)₂. As shown in Table 1, the
 12 surfactant has the same fluorocarbon chain as 6FS(EO)₂, but with an extra methylene unit

next to the headgroup, such modification on structure has been reported to enhance the water loading capacity effectively stabilize w/c microemulsions.³²

For the system with added C₈Benz, despite the enhanced stabilities compared to 6FS(EO)₂ systems, SANS results have also shown that thickness of the hydrocarbon-rich layer was reduced by ~45% (from 11 Å to 6 Å) in 6FG(EO)₂ stabilised microemulsions. Such a difference between 6FG(EO)₂ and 6FS(EO)₂ stabilised systems should be attributed to the additional methylene group in the hydrophilic region of the surfactant, as suggested by Sagisaka et.al,³² this introduces extra flexibility for surfactant packing at the interface.

System	Shell SLD / (10 ⁻⁶ Å ⁻²)	R _{core} /Å (±1 Å)	Thickness Shell /Å (±1 Å)	σ/R_{core}	[hydrotrope] / (mol L ⁻¹)
6FS(EO) ₂	3.5	18	8	0.18	-
6FS(EO) ₂ +C ₀ Benz	3.6	16	8	0.20	0.46
6FS(EO) ₂ +C ₀ Benz	3.6	15	8	0.25	0.23
6FS(EO) ₂ +C ₂ Benz	3.5	16	8	0.18	0.46
6FS(EO) ₂ +C ₂ Benz	3.4	15	8	0.24	0.23
6FS(EO) ₂ +C ₈ Benz*	3.5	13 11 (hydrotrope layer)	8	0.30	0.23
6FG(EO) ₂	3.5	17	8	0.18	-
6FG(EO) ₂ +C ₀ Benz	3.3	17	8	0.18	0.23
6FG(EO) ₂ +C ₂ Benz	3.5	15	8	0.21	0.23
6FG(EO) ₂ +C ₈ Benz	3.5	13 6 (hydrotrope layer)	8	0.28	0.23
4FG(EO) ₂	3.5	19	6	0.21	-
4FG(EO) ₂ +C ₀ Benz*	3.4	22	6	0.22	0.23
4FG(EO) ₂ +C ₂ Benz	3.6	13	6	0.30	0.23
4FG(EO) ₂ +C ₈ Benz	3.7	11 6 (hydrotrope layer)	6	0.35	0.23

Table 2. Important fitting parameters for hydrotrope free and different hydrotrope mixed w/c microemulsions with surfactants 6FS(EO)₂, 6FG(EO)₂ and 4FG(EO)₂. Data were obtained at 350 bar, 45°C.

***The system was turbid at stirring, the data were analysed for the clear phase with the stirrer stopped.**

In summary, the results have clearly indicated that, despite being expelled from the fluorocarbon shell, long chain hydrotropes tend to mix with the hydrocarbon moiety of the surfactant. But with a relatively constrained structures at the interface as obtained in the 6FS(EO)₂ stabilised systems, the hydrotropes suffer a greater entropy penalty, and therefore is located further from the surfactant layer. As unfavourable interactions increase between the hydrotrope alkyl chains and the sulfosuccinate groups in the surfactant, the systems also become relatively unstable.

3.3 Hydrotropes with 4FG(EO)₂: As compared in the previous section, reduction of surfactant chain length with only two CF₂ units on each tail appeared to result in significant effects on the stabilisation of w/c microemulsions with C_nBenz additives. SANS on 4FG(EO)₂ systems has shown that a sharp rise of low Q intensity was obtained for the microemulsions mixed with C₀Benz, consistent with the visual observation of large droplets even at the highest pressure (350 bar). However, the peak at medium Q corresponding to the core-shell interference was still obtained for both stirred and non-stirred (thus, a clear single phase) systems, which confirmed formation of a Winsor II type microemulsion.

With increased hydrotrope chain length, C₂Benz and C₈Benz formed stable mixtures with 4FG(EO)₂ stabilised w/c microemulsions. SANS results also showed similar behaviour for 4FG(EO)₂, 6FG(EO)₂ and 6FS(EO)₂ stabilised systems with C₂Benz hydrotrope. For the system with the long chain C₈Benz additive, however, SANS did not show strong evidence for the multi-shell structure as found in 6FS/FG(EO)₂+C₈Benz systems. Although by using the core multi-shell model, good fits could still be obtained, the hydrotrope layer thickness, however, cannot be determined with any precision. Moreover, the multi-shell model fitting cannot be

1 so readily distinguished from a single shell model (see Supporting information) as clearly as
2 found with the 6FS/FG(EO)₂ + C₈Benz systems.

3 Nevertheless, the scattering from the 4FG+C₈Benz system showed a notable increase of
4 background intensity compared with the hydrotrope free systems, which should be
5 attributed to increasing incoherent scattering from the hydrocarbon additives. Therefore,
6 the hydrotrope molecules might be held within the microemulsion droplets, otherwise the
7 ¹H containing compounds would be too dilute in the bulk phase ($\sim 7.5 \times 10^{-4}$ mol L⁻¹) to give
8 such a significant effect on incoherent scattering. Moreover, Hatzopoulos et al.¹⁸ have
9 demonstrated that the critical aggregation concentration (cac) of C₈Benz in aqueous
10 solution is 0.011 mol L⁻¹, whereas in this study, the concentration of hydrotrope in the
11 aqueous core was ~ 0.23 mol L⁻¹, thus, about 20×cac. At this concentration, such amphiphilic
12 molecules can be hardly dispersed in the aqueous core as normal solutes. Therefore, it is
13 reasonable to believe that the long chain hydrotrope C₈Benz should behave in the same way
14 regardless to the surfactant chain length.

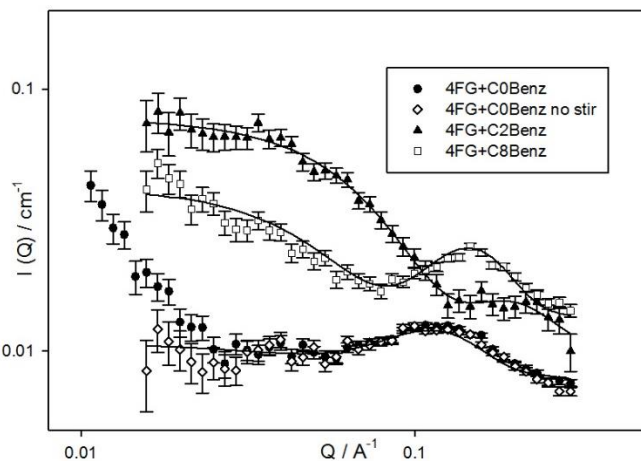
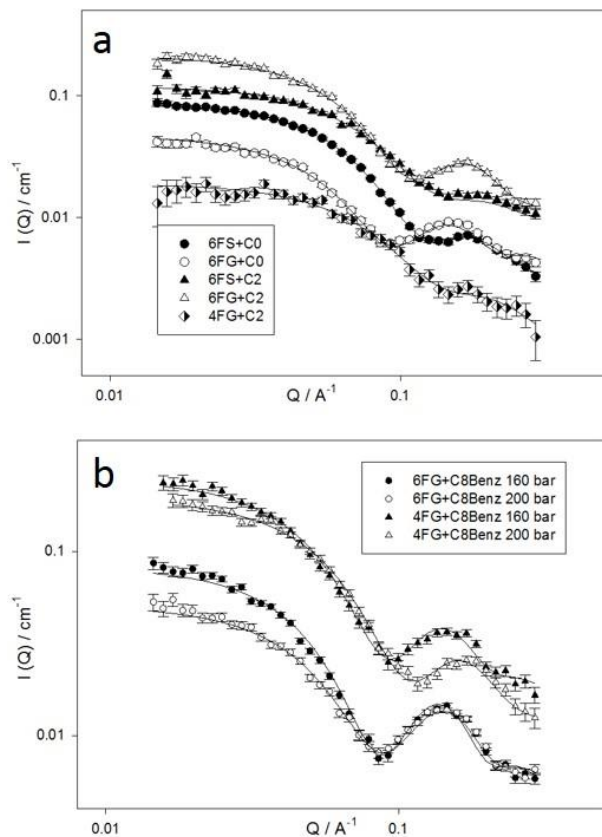


Figure 3. SANS results for 4FG(EO)₂ stabilised microemulsions with C₀, C₂ and C₈Benz. It should be noted that C₀Benz gives a turbid mixture with 4FG(EO)₂, SANS studies were performed while the system was being stirred and steady, and the results are compared. The systems with C₂ and C₈ hydrotropes have been multiplied by 3×.

From a series of w/c microemulsions with a similar contrast as applied in this study, Yan et al. have demonstrated that by either increasing the core size or decreasing surfactant chain length, the scattering from the core become more significant and the core-shell features become less apparent.²⁰ Furthermore, the SLD of the hydrotrope is very close to that for the core, and in 4FG(EO)₂ stabilised systems where the core-shell structure appears to be less pronounced, and therefore, to distinguish such a subtle structural feature is very difficult, especially within $\sim 5\text{\AA}$.

3.4 Effect of CO₂ density: The systems discussed in above sections were all obtained at 350 bar with the bulk density $\rho_{\text{CO}_2}=0.917 \text{ g cm}^{-3}$. In previous studies, it has also been revealed that variation of bulk density can result in significant effects on the film properties in w/c microemulsions and could even drive droplet shape transitions.²⁰ Herein, the structures of microemulsion droplets in the hydrotrope mixed systems, in particular, for those obtained from stable and clear phases, are compared at reduced pressure using SANS.

1



2

3 **Figure 4a (upper) compares the SANS from w/c microemulsions with two short chain**

4 **hydrotropes (C0 and C2) at reduced CO₂ density ($\rho_{\text{CO}_2}=0.812 \text{ g cm}^{-3}$, $P=200 \text{ bar}$ at 45°C).**

5 **The datasets for 6FS+C₂Benz and 6FG+C₂Benz systems have been multiplied by a factor of**

6 **3 \times . In 3b (lower), the structure has been compared between the 4FG and 6FG(EO)₂**

7 **stabilised microemulsions with C8 hydrotrope at reduced CO₂ density ($\rho_{\text{CO}_2}=0.812 \text{ g cm}^{-3}$,**

8 **$P=200 \text{ bar}$ at 45°C ; and $\rho_{\text{CO}_2}=0.759 \text{ g cm}^{-3}$, $P=160 \text{ bar}$ at 45°C), datasets for 4FG+C₈Benz at**

9 **160 bar has been multiplied by 4 \times , and the system at 200 bar by 5 \times .**

10 For a bulk density $\rho_{\text{CO}_2}=0.917 \text{ g cm}^{-3}$ at 350 bar, 6FS and 6FG(EO)₂ stabilised w/c

11 microemulsions with added short chain hydrotropes (C₀ and C₂Benz) appear to have similar

12 structures. However, as pressure is reduced to 200 bar ($\rho_{\text{CO}_2}=0.812 \text{ g cm}^{-3}$), a notable

1 difference is obtained for the two systems: as shown in Figure 4a, the definition of primary
2 and secondary peaks diminished with 6FS(EO)₂, consistent with a significant increase in
3 polydispersity. Whereas in 6FG(EO)₂ stabilised microemulsions, the core-shell features were
4 more clearly distinguished and little differences in structure are noted compared to the 350
5 bar case. On the other hand, for systems stabilised by 4FG(EO)₂, pressure variation appears
6 to affect the polydispersity, which increased from 26% to 32% as CO₂ density was reduced
7 from 0.812 g cm⁻³ to 0.759 g cm⁻³.

8 Once a longer chain hydrotrope (C₈Benz) was introduced to 4 and 6FG(EO)₂ stabilised
9 microemulsions, however, the effect of bulk density appears to be quite the opposite
10 compared short chain hydrotropes. Most notable is for the 6FG(EO)₂ system from 200 and
11 160 bar (ρCO₂=0.812 and 0.759 g cm⁻³ respectively), the scattering profiles interpreted in
12 terms of the core multi-shell model indicate increasing hydrotrope layer thickness, reducing
13 core radius and increasing polydispersity. Whereas for 4FG(EO)₂ stabilised systems, such
14 effects on the hydrotrope layer were not observed. It should be noted that the core multi-
15 shell model applied in these systems is based on a constant composition assuming 80%wt
16 hydrotrope coexists with 20%wt H₂O/D₂O in the hydrotrope layer, and the layer-thickness is
17 treated as a variable. Alternatively, if the hydrotrope layer thickness was set as a fixed
18 parameter, a decreased SLD_{hydrotrope layer} will be obtained corresponding to increasing
19 hydrotrope concentration in the co-existing water droplet phase. Nevertheless, results have
20 clearly revealed that the effect of bulk density on the adsorption of hydrotropes is more
21 significant in 6FG(EO)₂ stabilised microemulsions comparing to systems with 4FG(EO)₂,
22 which can be attributed to increasing effect of de-mixing between hydrotropes and
23 fluorocarbon surfactants. Comparison of the behaviour of C₈Benz in 4 and 6FG(EO)₂ seems

- 1 to suggest that, despite the similarity of structures at the headgroup, the surfactant with
 2 reduced CF₂ units is more miscible with the hydrotrope, which may be attributed to the
 3 reduced antipathy for the hydrocarbon species as the number of CF₂ units is reduced.

System	Shell SLD /10 ⁻⁶ Å ⁻²	R _{core} /Å (±1 Å)	Thickness Shell /Å (±1 Å)	σ/R_{core}	P CO ₂ / (g cm ⁻³)
6FS(EO) ₂ +C ₀ Benz	3.6	16	8	0.27	0.812
6FS(EO) ₂ +C ₂ Benz	3.2	13	8	0.34	0.759
6FG(EO) ₂ +C ₀ Benz	3.2	17	8	0.20	0.812
6FG(EO) ₂ +C ₂ Benz	3.4	19	8	0.23	0.759
4FG(EO) ₂ +C ₂ Benz	3.3	14	6	0.33	0.812
6FG(EO) ₂ +C ₈ Benz	3.5	11 11 (hydrotrope layer)	8	0.30	0.812
4FG(EO) ₂ +C ₈ Benz	3.7	12 6 (hydrotrope layer)	6	0.32	0.812
6FG(EO) ₂ +C ₈ Benz	3.5	7 15 (hydrotrope layer)	8	0.35	0.759
4FG(EO) ₂ +C ₈ Benz	3.8	16 6 (hydrotrope layer)	6	0.26	0.759

4 **Table 3 Important fitting parameters for different hydrotrope mixed w/c microemulsions**
 5 **with surfactants 6FS(EO)₂, 6FG(EO)₂ and 4FG(EO)₂ at reduced pressure with constant**
 6 **temperature 45°C.**

- 7 Although it has been suggested in a previous section that, the less apparent core-shell
 8 structures in 4FG(EO)₂ may result in difficulty in distinguishing the hydrotrope rich layer in
 9 such systems. However, if the hydrotrope molecules accumulate with a similar behaviour as
 10 in 6FG(EO)₂ systems, an effect should be eventually obtained, but that was observed for
 11 neither of the systems stabilised by 4FG(EO)₂ at reduced bulk densities.

4. Conclusions

The behaviour of hydrotropes have been investigated systematically in water-in-scCO₂ (w/c) microemulsions stabilised by a series of fluorocarbon surfactants: 6FS(EO)₂, 6FG(EO)₂ and 4FG(EO)₂.

In summary, w/c microemulsions can be influenced by hydrotrope additives in two ways:

firstly, the electrostatic interaction arising from hydrotrope ionization in the water pool, which in general will tend to destabilise microemulsions; and secondly, adsorption of hydrotrope molecules towards the water/surfactant/CO₂ interface. It should be noted that, consistent with a number of studies on hydrotropic behaviour in aqueous phases,^{33, 34} instead of an 'on-off' association switch seen with most classical surfactant systems, a stepwise association is preferred for hydrotropes over a range of concentration. In other words, even at concentrations above the cac, the effect of hydrotropes could be very different as the adsorption continues to increase at higher concentrations: this is expected to be achieved by longer chain hydrotropes.^{15, 21} However, as the hydrotrope becomes more 'surfactant-like' with increasing hydrophobicity, the mixture becomes less stable with increasing counteraction from the fluorocarbon moieties in the surfactant layer. Although contrast variation SANS has shown evidence for interfacial segregation of the surfactants and hydrotropes, the resolution of this technique is not high enough to enable further speculation regarding the relative orientations and distributions of the two components in the films.

Although only certain hydrotrope: surfactant ratios were considered, higher levels are more likely to induce elongated micellar structures, the results have clearly revealed the generality of the action of hydrotropes with microemulsions, both water-in-CO₂(here) and

1 water-in-hydrocarbon ^{15, 16} systems . Furthermore, the packing of hydrotropes into the
2 surfactant films has also emphasised the significance of surfactant headgroup structure.
3 Interactions between the hydrotropes and hydrocarbon moieties of the surfactants appear
4 to be key for affecting stability, and possibly structure, of the microemulsion droplets. Such
5 effects may not be limited to surfactant-hydrotrope systems as discussed in this study, but
6 can also be expanded to other additives, such as para-substituted phenols,^{35, 36, 37} which
7 have been demonstrated as effective viscosity modifiers in hydrocarbon systems through
8 formation of extended elongated micelles. By highlighting the similarities between self-
9 assembly of these surfactant-hydrotrope mixtures in scCO₂ and hydrocarbon solvents,
10 effective methods could be developed to improve the physicochemical properties of scCO₂,
11 which allows potential applications to be practically achievable.

12 **Acknowledgements**

13 C.J. acknowledges the EPSRC for postdoctoral funding through EPSRC EP/K020676/1 under
14 the G8 Research Councils Initiative on Multilateral Research Funding - G8-2012. J.P. thanks
15 the Science and Technology Facilities Council for a PhD scholarship ST/L502613/1.

-
- 1 Jarrell P.M., Fox C.E., Michael H., Webb S.L., SPE Monogr. Ser. 2002; 22: 21.
 - 2 Stalkup F. I., J. Petrol. Technol., 1983; 35: 815
 - 3 Lancaster G., Sinal M., Petroleum Society of CIM, 1986, Paper No. 86-37-69
 - 4 Sanders A., Jones R., Mann T., Patton L., Linroth M., Nguyen Q., 2010a. Successful implementation of CO₂ foam for conformance control. In: Proceedings of the 16th Annual CO₂ Flooding Conference. Midland, TX, December 8–10th
 - 5 Talebian S.H., Masoudi R., Tan I.M., Zitha P.L.J., Journal of Petroleum Science and Engineering; 2014; 120: 202.
 - 6 Trickett K., Xing D., Enick R., Eastoe J., Hollamby M. J., Mutch K. J., Rogers S. E., Heenan R. K., Steytler D. C., Langmuir 2010; 26: 83.
 - 7 Cummings S, Enick R, Rogers S, Heenan R, Eastoe J. Biochimie, 2012; 94: 94.
 - 8 Kutay S.M., Shramm L.L, Journal of Canadian Petroleum Technology, 2004; 43: 19
 - 9 Worthen A.J., Bryant S.L., Huh C., Johnston K.P., AIChE J. 2013; 59: 3490
 - 10 Adkins S.S., Gohil D., Dickson J.L., Webber S.E., Johnston K.P., Phys.Chem.Chem.Phys. 2007; 9: 6333
 - 11 Consani K.A., Smith R.D. J., Supercrit. Fluids 1990; 3: 51
 - 12 Eastoe J., Fragneto G., Steytler D.C., Robinson B.H., Heenan R.K., Physica B 1992; 180 & 181: 555
 - 13 Rakitin A.R., Pack G.R., Langmuir 2004; 21: 837
 - 14 Gaikar V. G.; Padalkar K. V.; Aswal V. K. J. Mol. Liq. 2008; 138: 155
 - 15 Hatzopoulos M.H., James C., Rogers S., Grillo I., Dowding P.J., Eastoe J.; Journal of Colloid and Interface Science 2014; 421: 56
 - 16 Hatzopoulos M.H., Eastoe J., Dowding P.J., Grillo I., Journal of Colloid and Interface Science 2013; 392: 304
 - 17 James C., Hatzopoulos M.H., Yan C., Smith G.N., Alexander S., Rogers S.E., Eastoe J., Langmuir 2014; 30: 96
 - 18 Lau C.; Butenhoff J.L.; Rogers J.M. Toxicol. Appl. Pharmacol. 2004; 198 ;231
 - 19 Houde M.; Martin J. W.; Letcher R. J.; Solomon, K. R.; Muir, D. C. G. Environ. Sci. Technol. 2006; 40: 3463
 - 20 Yan C., Sagisaka M., James C., Rogers S.E., Alexander S., Eastoe J., Journal of Colloid and Interface Science 2014; 435: 112
 - 21 Hatzopoulos M.H., Eastoe J., Dowding P.J., Rogers S.E., Heenan R., Dyer R., Langmuir 2011; 27: 12346
 - 22 Sagisaka M., Yoda S., Takebayashi Y., Otake K., Kondo Y., Yoshino N., Sakai H., Abe M., Langmuir 2003; 19: 8161

-
- 23 Span R. Wagner W., J. Phys. Chem. Ref. Data, 1996; 25: 1509
- 24 Heenan R.K., Rogers S.E., Turner D., Terry A.E., Treadgold J.K., Neutron News 2011; 22: 19.
- 25 Wignall G D, Bates F S, J. Appl. Crystallogr. 1987; 20: 28.
- 26 King S M, Pethrick RA & Dawkins JV (editors), Modern Techniques for Polymer Characterisation, 1999; Chapter 7.
- 27 Guinier A., Fournet G., Wiley J., Small-Angle Scattering of X-Rays, 1995.
- 28 Kotlarchyk M., Chen S. H., J. Chem. Phys., 1983; 79: 2461.
- 29 Safran S.A., J. Chem. Phys., 1983; 78: 2073
- 30 Milner ST, Safran SA, Phys. Rev. A, 1987; 36: 4371
- 31 Leung R., Shan D.O., Journal of Colloid and Interface Science, 1987; 120: 330
- 32 Sagisaka M., Iwama S., Hasegawa S., Yoshizawa A., Mohamed A., Cummings S., Rogers S. E., Heenan R. K., Eastoe J., Langmuir, 2011; 27: 5772
- 33 Balasubramanian D., Srinivas V., Gaikar V. G., Sharma M. M., J. Phys. Chem. 1989; 93: 3865
- 34 da Silva, R. C., Spitzer, M., da Silva, L. H. M., Loh W., Thermochim. Acta 1999; 328: 161
- 35 Xu X., Ayyagari M., Tata M., John V. T., McPherson G. L., J. Phys. Chem., 1993; 97: 11350
- 36 Singh M., Tan G., Agarwal V., Fritz G., Maskos K., Bose A., John V., McPherson G., Langmuir, 2004; 20: 7392
- 37 Simmons B. A., Taylor C. E., Landis F. A., John V. T., McPherson G. L., Schwartz D. Moore K. R., J. Am. Chem. Soc., 2001; 123: 2414